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Emissions of Vapor-Phase Fluorine and Ammonia from the Columbia Coal-Fired Power Plant

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JOURNAL ARTICLE

Emissions of Vapor-Phase Fluorine and Ammonia from the Columbia Coal-Fired Power Plant

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■ Gaseous fluorine and ammonia emissions from two pulverized-coal power plants were measured over a 6-month period. In one unit, emissions contained a median 1.5 mg/scm (standard cubic meter) NH_3 and 1.9 mg/scm F (86% of available F in coal). For the other unit lower levels were found: 0.042 mg/scm NH_3 and 0.22 mg/scm F (4.2% of available F in coal). Ammonia varied by more than 10 times in each unit and was enhanced in Unit I by addition of ammonium carbonate to improve precipitator efficiency. Fluorine varied less than 50% in each unit. The difference in F between units was related circumstantially to ash content. Daily variation of F and NH_3 was less than 20%. Neither gas was in sufficient quantity relative to SO_2 to influence net acidity. Levels of F were comparable to those of other combustion sources and the aluminum industry. On a global scale, coal combustion is not a major source of either F or NH_3. Among anthropogenic sources, however, it is a significant contributor and may be important locally. In contrast, NH_3 emissions are negligible.

Introduction

Among the atmospheric emissions from coal-fired power plants are several major vapor-phase materials having important environmental impacts: CO_2, SO_2, and NO_x. In addition, a number of trace materials in coal seem to be emitted largely as vapors, notably, Hg, Se, Cl, Br, and F (*1–4*). Knowledge about these trace gases has been derived indirectly from discrepancies in mass balances; particulate emissions cannot account for all of the mass that entered in the fuel. Lack of direct data for minor gas species is most often due to the necessity for individualized sampling and analysis methodology. Considerably more effort must be expended in a study of trace gases than in a particulate matter emission study. Consequently, it is not surprising that previous work has focused primarily on major gases and particulate emissions, for which integrated sampling and analysis schemes (e.g., inertial impaction and neutron activation analysis) provide data on many elements simultaneously.

Since flue gas chemistry and emission factors of minor vapor species represent gaps in our knowledge, this research studied two neglected materials, F and NH_3. Our purpose was (1) to evaluate sampling and analysis methodologies for vapor-phase fluorine and ammonia, (2) to determine flue gas concentrations for emission inventory estimates, (3) to determine short- and long-term variability, and (4) to compare coal-fired steam plant NH_3 and F atmospheric emissions with other anthropogenic and natural sources.

The plant studied was the Columbia electricity generating station in Portage, WI. The station consists of two 527-MW pulverized-coal furnaces. Unit I, which came on line in the early 1970s, has a 107-m stack and was burning a western bituminous coal (Colstrip, MT) containing 9% ash and 1% S (dry coal basis). Unit II, which came on line in the mid-1970s, has a 198-m stack and was burning another bituminous coal (Gillette, WY) containing 5% ash and 0.7% S. The Columbia station offered a unique opportunity to compare two nearly identical combustion units, differing only in type of coal burned and operating conditions.

Experimental Section

General Sampling Procedures. Research Appliance Co.'s "Staksamplr" (Model 2414) with a 1.5-m heatable glass probe was used to collect gas samples. The rest of the sampling train consisted of a cyclone and filter holder encased in a heatable box, an ice bath containing four impingers in series, and the meter case, consisting of manometer, pump, and dry gas meter bracketed by thermometers. An "S" type pitot tube was used to measure flue gas velocity. All surfaces contacting the sampled gases were glass except for the filter holder, which contained a plastic support for the glass frit.

Glassware was scrubbed with Alconox, soaked in hot nitric acid, and rinsed with distilled deionized water. Nalgene linear polyethylene bottles used for impinger collection solutions were leached for a week with dilute reagent-grade HCl and rinsed with water.

Sampling was performed within one of two horizontal ducts leading to the stack. Each duct had several sampling ports, one of which was selected to obtain all samples. This port was situated away from bends in the ducts to minimize gas flow inhomogeneity. Stack gas temperature was measured by means of a thermocouple attached to the pitot tube. Stack pressure, measured by means of a water manometer, was always within 2.5 ± 1.2 cm of water from atmospheric pressure. The first two impingers were each filled with 100 mL of the appropriate collection solution from sample bottles previously filled in the laboratory. The third impinger contained 3% sodium carbonate solution to protect the pump from corrosive vapors. The fourth impinger was dry. The probe and filter compartment were heated to between 60 and 80 °C. During sampling, the probe and filter case were observed to be free of condensation.

After sampling, impinger solutions were transferred quantitatively back into their storage bottles. Volumes were measured at the laboratory by using calibrated graduated cylinders. The combined volume gain for all impingers during the day was used to calculate water vapor content of the stack gas. Samples were stored at 4 °C. Even after several months of storage, volumes remeasured for selected bottles showed no changes.

Fluorine Sampling. Methods have been reported for distinguishing particulate and vapor-phase F in the atmosphere (*5–10*) and in emissions from aluminum refining (*11, 12*) and fertilizer production (*8, 13*). Coal combustion emissions have not been given much attention despite estimates indicating that they represent one of the major industrial sources of atmospheric F (*10, 14*).

The method of Dorsey and Kenmitz (*15*) was adopted after modification. It involves collection through a hot glass probe, in which HF is transformed quantitatively into

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SiF_4 at the probe walls. Being less reactive than HF, SiF_4 will pass through a filter without being trapped, thus effecting separation of particulate and vapor-phase F. The gas is then bubbled through impingers containing aqeuous NaOH, where SiF_4 is hydrolyzed to soluble fluoride. Just in case conversion to SiF_4 was not complete in the probe, we used a citric acid impregnated paper filter (Whatman 42) (*5*) instead of glass fiber (*15*). A rate of 0.02 m^3/min was used, and probe and filter box temperatures were hot enough to keep the relative humidity below the recommended maximum (*6*) of 90%. Accuracy of particle/vapor separation was not tested in this laboratory. Under these conditions, approximately 1–2 m^3 of gas had to be collected to provide adequate fluoride for analysis.

Quantitative collection of SiF_4 and HF has been achieved in 0.1 M NaOH (*13*, *15*), but we selected 0.75 M NaOH so that the major acidic gases, namely, CO_2, SO_2, and NO_x, would be neutralized. Acidic conditions were avoided to prevent possible loss of F as HF. None of the field samples had a pH below 10 after collection.

This method does not distinguish between HF, SiF_4, and H_2SiF_6, any of which might exist in the flue gas. All of these forms will be collectively referred to as "fluorine" or "fluoride".

Fluoride Determination. Fluoride was determined potentiometrically by standard additions by using an Orion F-selective electrode (Model 94-09A), an Orion double-junction Ag/AgCl reference electrode (Model 90-02), and an Orion Model 801 digital meter. Electrode response was determined each analysis day by construction of a working curve. Two different complexing buffer solutions were used with equivalent effect: cyclohexylenedinitrilotetraacetic acid in acetic acid/acetate buffer (*5*, *16*), and citric acid/citrate in ammonium/ammonia buffer (*8*, *16*). Dry reagent-grade NaF was dissolved in 50% buffer for stock fluoride standard. Standards and buffers were stored at 4 °C. Polyethylene labware was used.

A 25-mL aliquot of each sample solution was transferred by pipet to a beaker along with an equal volume of buffer; a measured volume of glacial acetic acid was added to bring the pH to 5.5–6.0. This acidification caused loss of CO_2 absorbed from the stack gas. The beakers were covered and stirred until effervescence had subsided. Fluoride response was determined in duplicate from two standard addition spikes into one aliquot of sample.

Coal. Lump coal was collected in kilogram quantities from all the hoppers that fed the pulverizers. Representative 30-g analytical samples were prepared (*17*). Fluoride determinations were performed by CDM/Accu-labs in Wheat Ridge, CO, using ASTM Method D3761.

Ammonia Sampling. Dilute sulfuric acid (0.5 M) has been reported to be an efficient absorbent for atmospheric NH_3 (*18*). A gas sampling rate of 0.025 m^3/min and a stack gas total volume of 1.4 m^3 were used. Two glass-fiber filters were placed in the sampling train. These were leached first with sulfuric acid to neutralize excess alkalinity (*19*, *20*) and then with water until acid free to help avoid the conversion of ammonium salts to ammonia.

The sampling train illustrated in Figure 1 was used to determine whether ammonia would pass quantitatively through the filters. Known quantities of ammonia were generated and passed through the train under conditions similar to those used for stack gas sampling. The vapor source was 150 mL of 1.25×10^{-3} M NH_4Cl in 0.5 M H_2SO_4. The two collection impingers and the inlet impinger each contained 100 mL of 0.5 M H_2SO_4. When the solution in the source impinger was made basic and ambient air was pulled through the train, ammonia vapor

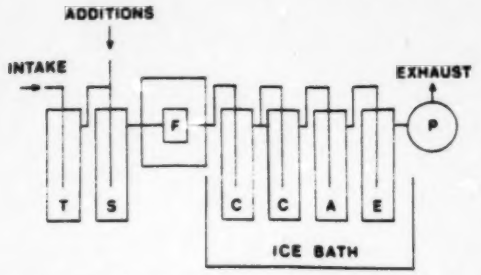

Figure 1. Apparatus for test of ammonia sampling train. F = filter holder in heated cabinet; P = pump; T = inlet trap, dilute H_2SO_4; S = source impinger, acidic ammonia solution; C = collection solutions, dilute H_2SO_4; A = alkaline trap for pump protection, dilute sodium carbonate; E = empty.

from the source was transported through the system. Ammonia concentrations in the source solution before and after "sampling" and in the collection impingers were measured. The inlet impinger absorbed any ammonia present in laboratory air and conditioned the air with respect to water vapor and acid vapor so that the source impinger would not be stripped of its contents.

Several different obstacles were placed between source and collection impingers: (1) a glass connector, (2) two neutralized, clean, glass-fiber filters heated to between 50 and 70 °C, or (3) a filter laden with 190 mg of fly ash from a stack sampling run, also heated to between 50 and 70 °C. Enough 10 M NaOH was added to the source impinger to raise the pH above 11 and release NH_3. The pumping rate was then increased to 0.025 m^3/min, the rate used for stack gas sampling. After 0.8 m^3 had been passed, H_2SO_4 was added to the source to stop NH_3 evolution. Bubbling was continued for another 0.15 m^3 to purge the source of remaining ammonia.

Ammonia Determination. Ammonia was determined potentiometrically by standard additions with an Orion Model 95-10 NH_3 gas electrode and an Orion 801 meter. Electrode response was determined each analysis day. All chemicals were reagent grade. Ammonia standards were prepared from dry NH_4Cl dissolved in 0.5 M H_2SO_4.

A 25-mL aliquot of each sample was transferred by pipet to a beaker along with an equal volume of water. After the beaker was chilled in a cold water bath (4–10 °C), 10 M NaOH was added from a buret until the pH exceeded 11.5, as determined by using a glass electrode. The beaker was then covered and placed in a room temperature water bath for 5 min. The NH_3 electrode was immersed in the magnetically stirred sample, and the response was recorded after 5 min. No loss of NH_3 was noted as indicated by absence of drift in electrode response during the time span of the measurement. Duplicate determinations were made on the basis of two standard addition spikes into a single aliquot of sample. Additional pH measurements made after these additions of acidic standard indicated that pH remained above 11.

Temperature control is necessary for reproducible response. This was especially important because entrapment of water vapor and acid gases from the stack caused varying acidities in the collection solutions. Without control, addition of base raised temperatures variably and as high as 40 °C.

Results and Discussion

Collected Samples. Samples were collected 6 times in each combustion unit between April and Oct 1980. Two of these samples were collected the same day several hours apart.

Concentrations of F ranged from about 0.3×10^{-4} to 5×10^{-4} M in the first impinger and from 0.3×10^{-5} to 1.5×10^{-5} M in the second; for ammonia, the concentrations ranged between 10^{-6} and 10^{-3} M in the first impinger and between 10^{-6} and 10^{-4} in the second. Reagent blank levels were about 10^{-6} M for both F and NH_3. Analytical precisions, whether F or NH_3, were about 5% relative standard deviation for the first impinger and about 20% for the second impinger. Since masses collected in the first impinger were usually much greater than those in the second, the net error in the sum is about 5%.

Accuracy of Fluoride Method. Loss of dissolved F^- in the glass impingers was tested by stirring a known concentration of sodium fluoride dissolved in 0.75 M NaOH collection solution in a glass beaker for 75 min. Fluoride determinations were performed on aliquots of solution before and after contact with the glass. At 10^{-4} M F^- (typical of the first impinger) no losses were observed; however, at 10^{-5} M (second impinger) about 15% was lost. Although significant for impinger 2, this loss was negligible for the sum of impingers 1 and 2 for all samples.

Previous literature indicated (*13*) that collection of water-soluble fluorine species by simple impingers should be nearly quantitative. Our field sampling results generally supported this observation; the second impinger was found to contain a median value of 3.2% F compared to the first, with a range of 0.8–17.1%.

Accuracy of Ammonia Method. Ionic strength of sample solutions is an important consideration in achieving stable electrode response. Addition of concentrated base to the 0.5 M H_2SO_4 collection solutions to release ammonia resulted in ionic strengths of nearly 3 M. This solution required about 30 min of stabilization time apparently because osmotic pressure forced water out of the internal filling solution (about 0.1 M NH_4Cl). Equilibration times were measured for the electrode when immersed in solutions of 2.3×10^{-4} M NH_4Cl containing varying ionic strengths. Ionic strengths of 0.3, 0.6, and 1.4 M required less than 5 min for equilibration, whereas an ionic strength of 2.7 M (undiluted sample solution) lengthened the time to 25 min. All sample solutions, therefore, were diluted one-to-one with water just before analysis to reduce equilibration time to 5 min.

An additional concern was the possibility that metal ions might complex NH_3 irreversibly, thus causing low results. Most metals are particulate associated and should be removed by the filter. Only volatile Hg^0 might penetrate substantially. Furthermore, Hg(II) forms a fairly strong ammonia complex ($pK_1 = pK_2 = 9$). Ammonia responses were measured in solutions containing 4×10^{-5} M ammonium and Hg(II) concentrations as high as 1.3×10^{-4} M. There was no apparent effect. This ammonium concentration was low compared with most of the stack sample solutions, and the Hg concentrations were chosen by estimating the amount available in typical coal combustion gases (*1*, *2*) and assuming complete oxidation to Hg(II).

Collection efficiency of NH_3 in the impingers and the effect of filtration are displayed in Table I. Each of the three treatments (no filter, clean filter, and fly ash laden filter) were duplicated, and each value listed is the average of two potentiometric determinations on each solution. The first three columns indicate where ammonia was found after the experiment had been completed. These columns should sum to 639 μg, the initial mass in every case. Analysis of variance indicated that recoveries for the three treatments were not significantly different at the 95% probability level; the overall mean recovery was 88 ± 6%. This 6% error can be attributed entirely to the analytical measurement. The reason why ammonia was "lost" has not been determined; however, the size of the discrepancy was not so severe as to compromise the accuracy of results for stack samples. Calculations of ammonia content of stack gas emissions included a 12% correction for collection efficiency.

Table I. Efficiency of Ammonia Collection and Effect of Filtration on Recovery

	mass of NH_3 found, μg				
	imp 1	imp 2	used std	recovery, %[a]	impinger ratio, %
no filter	506	13	76	93	2.5
	462	6	48	81	1.3
				87[b]	
clean filter	446	1	79	82	0.2
	511	3	55	89	0.6
				86[b]	
ash on filter	541	0	35	90	0.0
	557	2	50	95	0.4
				92[b]	
grand mean				88 ± 6	

[a] Sum of first three columns divided by 639; as percent. [b] Mean.

Table II. Comparison of Methods for Determining Stack Gas Flow Rates (in 10^6 dry scm/min)

Unit I		Unit II	
plant data	this work	plant data	this work
4.3	1.7	4.0	3.6
3.8	1.8	4.0	4.0
6.7	1.7	2.8	3.6
6.1	1.7	2.5	3.6
6.0	1.7	2.3	3.9
4.2	1.8	2.2	4.0

Table I also shows that the amount of ammonia reaching impinger 2 was negligible compared with the amount in impinger 1. Field sampling results, summarized above, were similar to the laboratory test results in most cases: the second impinger contained a median of 2.8% as much ammonia as the first impinger, with a range of 0.7–28%. High values were found only for those samples containing very little ammonia.

Emissions. Ammonia emission rates and concentration in the emitted gas were of primary interest. For F the amount appearing in the vapor phase relative to the amount input in the coal was also determined.

A factor of major importance was the means by which total stack gas flow was determined. Although stack gas velocity was measured each sampling day by means of a pitot tube, we were concerned whether this measurement was representative because Columbia plant records showed that flow velocities across the flue gas ducts were quite heterogeneous, with a variability of about 30%.

Another approach using plant records of SO_2 emissions was evaluated. The average flow rate was calculated each sampling day from SO_2 stack gas concentrations, measured by on-line monitors, and SO_2 mass emission rates, recorded hourly in plant records. The advantage to this approach was that these emission rates were calculated from an algorithm based on the average of gas velocity measurements at many points in the stack. This algorithm had been developed when each unit was evaluated for initial compliance with emissions regulations. Table II shows that gas flow rates determined from plant data and with our pitot measurement on the same day are substantially different.

Table III. Concentrations and Emission Rates of Ammonia at Columbia Coal-Fired Power Plant

date	μg/scm	kg/h	ppm
	Unit I		
4/17	1700	4.3	2.6
5/29	11000	25	16
9/3	6300	26	9.5
9/5	1000	3.7	1.5
9/5	1400	5.1	2.1
10/20	250	0.63	0.4
median	1550	4.7	2.3
	Unit II		
date	μg/scm	kg/h	ppb
6/24	11	0.026	16
6/26	0.6	0.001	0.9
7/21	75	0.13	110
7/24	131	0.20	200
10/24	46	0.060	69
10/24	42	0.056	63
median	42	0.056	66

Table IV. Concentrations, Emission Rates, and Mass Balance of Vapor-Phase Fluoride at Columbia Coal-Fired Power Plant

date	mg/scm	kg/h	F emitted as vapor, %	stack temp, °C
		Unit I		
4/17	2.9	7.4	87	137
5/29	1.6	3.6	50	156
9/3	1.8	7.4	85	144
9/4	2.0	7.3	94	149
9/4	2.2	8.0	102	149
10/20	1.5	3.8	22	132
median	1.9	7.4	86	
		Unit II		
6/24	0.15	0.36	4.0	189
6/26	0.16	0.38	4.3	184
7/21	0.34	0.57	5.9	165
7/24	0.25	0.37	3.8	160
10/22	0.23	0.32	4.7	157
10/22	0.20	0.28	4.2	157
median	0.22	0.36	4.2	

To determine which method was more accurate, a mass balance on carbon was calculated. Knowing the coal feed rate (hourly plant record), the percent carbon in the coal (determined daily by plant personnel using ASTM procedures), the concentration of CO_2 in the stack gas (hourly plant record), and the total gas flow rate, one can compare the C input and output rates. Correct gas flow rates should lead to a 100% C balance. The only assumption is that all of the C in coal be converted to CO_2. This is quite reasonable since emissions of CO and of unburned coal particles are negligible. Feed rates were corrected for coal moisture content, determined by plant personnel using ASTM procedures.

By use of stack gas flow rates calculated from SO_2 emissions, 95% of the C in the coal was accounted for (range 91–103%), in both combustion units. These values are accurate within about 20% because of propagation of error through the various calculations. Thus, flow rates calculated from SO_2 emissions are indeed accurate. In contrast, if values measured by pitot (Table II) had been used, mass balances would have been incorrect by as much as a factor of 3.

Stack gas concentrations and mass emission rates for ammonia and vapor-phase fluorine are listed in Tables III and IV, respectively. On all sampling days the combustion units were operating near full capacity, consuming about 2×10^5 kg of dry coal/h. Propagated uncertainties in the data in these tables range from 20 to 30%. Medians are displayed instead of means because shapes of the distributions of these variables were not known and individual values varied several orders of magnitude. Unit I emitted substantially higher concentrations of ammonia and vapor-phase fluoride than Unit II and at substantially greater rates. Note that samples collected the same day were much more similar to each other than those collected on different days.

Unit I had much larger emissions of ammonia because ammonium carbonate was added to improve particulate collection efficiency in the electrostatic precipitators. Ammonium carbonate decomposes at about 60 °C to NH_3, H_2O, and CO_2. Volume concentrations were somewhat less than expected (10–20 ppm) for this type of flue gas treatment (*22*). Since no additions were made to Unit II, the concentrations observed here indicate that modern pulverized-coal combustion produces very little ammonia. In addition, with SO_2 levels typically around several hundred ppm, there was not nearly enough ammonia to achieve significant acid neutralization, even in Unit I where ammonia had been added.

For F one could hypothesize that differences arose between units because of differences in the amount or nature of F within each coal or in combustion or stack gas chemistry. No significant difference existed between the F contents of the coals: Unit I's coal contained on average 46 ppm and Unit II's, 45 ppm. With regard to the form of F, this element occurs in coals predominantly in the inorganic minerals fluorapatite, $Ca_{10}F_2(PO_4)_6$, and fluorspar, CaF_2 (*10, 21, 23, 24*). (Fluoride mineralogies of the Columbia coals were not investigated in this project.) Whereas F can be volatized to a much greater extent from fluorspar than fluorapatite, Crossley (*25*) has shown that other minerals in the coals modify this behavior greatly. In particular, quartz promotes formation of gaseous SiF_4 (*10, 26*). Since Unit I coal had nearly twice the ash content of that in Unit II, the extra mineral matter may have played a role in the greater release of fluorine to the vapor phase in Unit I.

There is no indication that the higher ammonia levels in Unit I played a role in creating the higher F levels there. Tables III and IV show no apparent correlation between these two species. Table IV also shows that there was no clear relationship between flue gas temperature and amount of F in the vapor phase.

A few measurements of vapor-phase F emissions from other combustion sources are available for comparison. These are listed in Table V along with emission values from aluminum smelting operations. Columbia Unit I had emission concentrations similar to those for the other combustion sources. Levels in Unit II were somewhat lower, being more comparable to aluminum industry emissions. It should be noted that because of the significant amount of Fe released to the vapor phase by coal combustion, receptor modelers may be able to use vapor-phase F as a tracer for this source.

The form of F in the stack gas is likely to be either HF or SiF_4 (*10*). Our sampling system would have collected both species but was incapable of distinguishing between them. Upon emission to the atmosphere, the stack gas will have cooled sufficiently for water vapor to condense. Consequently, SiF_4 might hydrolyze to fluorosilicic acid (H_2SiF_6). The contribution of these two weak acid species to the overall acidity of the emissions was negligible. For

Table V. Comparison of Fluorine Emission Sources

source	emitted concn, mg/scm[a]	F emitted as vapor, %	ref
coal			
pulverized (6)[b]	1.9 (1.5–29)	86	Unit I
pulverized (6)	0.22 (0.15–0.34)	4	Unit II
spreader-stoker (12)		91[c]	4
spreader-stoker (12)		98[c]	4
fluidized-bed (5)	10		27
municipal waste			
incinerator (9)	4.7 (1.9–25)		28
incinerator (9)	2.1 (1.2–3.0)		29
aluminum			
refinery	0.33 (0.13–1.2)		11
refineries[d]	(0.25–1.4)	40–70	30
unspecified		0.7–96	15

[a] Medians or means, with ranges in parentheses. [b] Number of samples. [c] Inflated slightly by inclusion of particulate matter that escapes to atmosphere (0.18% of total particulate). [d] Industry-wide average.

the two units, the median concentrations of 0.22 and 1.9 mg of F/scm were equivalent to roughly 0.3–3 ppm of F, whereas SO_2 concentrations were typically several hundred ppm.

To place these emission measurements into perspective, one should compare F and NH_3 emissions from coal combustion with those from other industrial and natural sources. Given a total U.S. coal consumption by electric utilties of about 5.4×10^{11} kg/year (*31*) and multiplying by an average F content of about 70 mg/kg (*21*), the total amount of F liberated by coal combustion is about 37×10^6 kg/year. Our data indicated that in typical pulverized fuel combustion as much as 95% and as little as 5% of this amount will be emitted as vapor-phase F species. This is roughly equivalent to previous estimates that place total particulate and vapor emissions from coal, based on an assumed 50% release of F to the atmosphere, at 15×10^6 (*10*) and 25×10^6 kg/year (*14*). At these levels coal combustion represents about 15% of the total domestic F emission (*10*, *14*). On a global scale, coal and other anthropogenic sources are minor compared to annual natural emissions of about 2.5×10^{10} kg (*32*); consequently, F pollution effects are likely to remain a local concern, as they have in the past.

Global ammonia emissions from coal combustion have been reported previously to be less than 2×10^9 kg/year (*33*), an insignificant amount compared with the dominant anthropogenic source—domestic animal feedlots at 23×10^9 kg/year (*33*)—and negligible compared with natural emissions at 1×10^{12} kg/year (*34*). Our measurements confirm this situation: assuming Unit I to be typical of the U.S. coal-burning utility industry, no more than 6×10^7 kg/year of NH_3 would be emitted in the U.S.

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